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13. ABSTRACT ***(Maximum 200 Words)***

Research accomplished and published on deterministic and stochastic behavior of systems far from equilibrium is summarized. Topics treated include: Long term variations of chemical systems with time-dependent rate coefficients; transit time distributions for such systems; stochastic potential for oscillatory systems; Anderson localization for reaction-convection systems; dynamics and dissipation in externally forced systems; rate processes with dynamic disorder; and linear free energy relations for systems with static and dynamic disorder.

14. SUBJECT TERMS

Non-linear irreversible systems, chemical kinetics, deterministic and stochastic behavior, dynamical disorder

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"Theory and Experiments on Chemical Instabilities"
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Deterministic and stochastic asymptotic behavior for non-equilibrium chemical systems with time-dependent rate coefficients, as in atmospheric reactions, has been investigated. There is an interesting new affect of such systems coming to a normal solution which is independent of the initial conditions. The second area of study has been the transition and transit times of intermediates in chemical reactions in an open system, and how measurements of such quantities, for instance by tracer experiments, yield information about the reaction mechanism. Stochastic potentials in externally perturbed limit cycles (oscillatory reactions) have been investigated and first order solutions of stochastic equations for such systems have been analyzed in detail. Another area investigated has been that of multi-component reaction convection chemical systems characterized by time-dependent but space-independent propagation velocities and find Anderson localization. Yet another study of oscillatory chemical systems is that of the imposition of colored noise which shows that even for small noise levels limit cycle oscillations can be dampened substantially. Work is nearly completed on a study of reaction-diffusion systems in which selection criteria for the types of patterns to be formed past a Turing instability are provided.

1. Deterministic and stochastic asymptotic behavior for nonequilibrium chemical systems with time - dependent rate coefficients

Long time limit of the nonequilibrium solutions of a system of multivariable nonlinear kinetic equations with time-dependent rate coefficients, as achieved, for example, by temporal variation of the temperature is being analyzed. If the characteristic time scale attached to the change of rate coefficients is smaller than the relaxation time to equilibrium, then the system is constrained to evolve away, possibly far from equilibrium. However, after a sufficiently large time the system forgets its past: in the long run all solutions of the kinetic equations tend towards a special (normal) solution which depends on the previous values of the rate coefficients but it is independent of the initial state of the system. The normal solution may be very different from the equilibrium solution. The occurrence of this type of time-dependent normal regime for the deterministic kinetic equations is intimately connected to a similar behavior of the stochastic evolution equation of the system. In the long run all solutions of the stochastic equation for the state probability also tend towards a normal form which is independent of the initial preparation of the system. The logarithm of the normal form of the state probability is a Lyapunov function of the system of deterministic kinetic equations and plays the role of a generalized thermodynamic potential which may be used for developing a thermodynamic description of the chemical process. A Gibbsian ensemble description is introduced in terms of a multi-replica

stochastic master equation. The logarithm of the large time solution of the multi-replica stochastic master equation is also a Lyapunov function, one for the stochastic evolution equations of the system . A kinetic experiment is suggested for checking the existence of normal solutions for chemical systems with time-dependent rate coefficients. This work has been published in the J. Phys. Chem. (355).

2. Transition and transit time distributions for time dependent reactions with application to biochemical networks

Temporal aspects of the dynamic behavior of biochemical pathways in stationary states have been described by a *transition time* t, which is the ratio of the sum of the pool concentrations of chemical intermediates to the flux for a given stationary state. In this paper, a related random variable is introduced, the *transit time* θ, which is defined as the age of (metabolic) intermediates at the time of leaving the system. The theory, based on a semi-stochastic approach, leads to calculations of the probability distributions of the ages of the intermediates, as functions of time. By assuming that the kinetics of the pathway is described by mass-action laws, a system of partial differential equations is derived for the distribution function of the transit time. By using the method of characteristics the solving of the evolution equations for the distribution function is reduced to the solving of the kinetic equations of the process. The method is applied to a simple enzyme-substrate reaction operated in two different regimes: 1) with a constant input of reagent and 2)with a periodically varying input. In the first case the transit time probability distributions in the steady state are calculated both analytically and numerically. The mean transit time, calculated as the first moment of the distribution, coincides with the transition time calculated in the literature. In addition, the presented approach provides information concerning the fluctuations of the transit time. For a periodic input the distribution function of transit times can be evaluated semi-analytically, by using the technique of Green functions. The distribution oscillates in time, and both the distribution of the transit time and its different moments and cumulants oscillate are shown in this case. This work has been published in J. Phys. Chem. (358).

3. Stochastic potential for a periodically forced nonlinear oscillator

Stationary and nonstationary probability densities for a weakly forced nonlinear physical or chemical oscillator system using a master equation approach are being investigated. The period and amplitude of forcing are taken as adjustable constraints. Our method of solution is based on the WKB expansion of the probability density with the system size as the expansion parameter. The first order term

in this expansion is a Hamilton-Jacobi equation for the stochastic potential (eikonal). The problem can be recast as a finite dimensional Hamiltonian system by the method of characteristics. Using the method of multiple time scales and Fredholm alternative, these equations are reduced to a two-dimensional Hamiltonian system in action angle variables. From solutions to this equation, the global stochastic potential is constructed on the invariant 2-torus of the deterministic system is constructed. The potential near the 2-torus is approximated by that for the limit cycle of the autonomous system. For parameter values within an entrainment region, the stationary potential on the 2-torus has a minimum on the entrained solution and exhibits a plateau, which is related to a nonzero average relative phase slippage (probability current). The potential on a cross-section of the 2-torus (in a Poincaré map) is equivalent to that of a Brownian particle in a periodic potential with a constant external force in the strong damping and weak noise limits. For parameter values outside of an entrainment region (for which a quasiperiodic solution exists on the 2-torus), the stochastic potential on the 2-torus is identically zero. For this regime, the evolution of an initially localized density is investigated on a cross-section of the invariant 2-torus. The width of this distribution grows proportionally with the square root of time; the proportionality factor depends upon both the position (phase) on the cross-section of the peak of the density and the distance in parameter space from the boundary of the entrainment region. For parameter values that approach the boundary of an entrainment region, this proportionality factor tends to infinity. An expression for the first order correction to the stochastic potential for both entrained and quasiperiodic solutions is determined. A thermodynamic interpretation of these results is made possible by the equality of the stochastic potential with an excess work function. This work has been published in the J. Chem. Phys. (359).

4. H-theorem for lifetime distributions of active intermediates in nonequilibrium chemical systems with stable limit cycles

The large time behavior of the lifetime distributions of active intermediates is investigated for nonequilibrium chemical systems with stable limit cycles. The lifetime distributions are the solutions of a system of partial differential equations which can be integrated by using the method of characteristics. A generalized H-function is defined in terms of two sets of solutions of these partial differential equations corresponding to two different initial solutions. A general H-theorem is proven which shows that for a system with a stable limit cycle all transient lifetime distributions evolve towards the same normal form which is a periodical function of time and is independent of the initial conditions. A frequency response tracer experiment is

suggested for the evaluation of the probability distribution of the lifetime of an intermediate. A special experimental setting makes possible the direct measurement of the Fourier transform of the probability distribution with respect to the lifetime of a molecule. This Fourier transform is a generalized susceptibility function which depends both on time and frequency. It is shown that the real and imaginary parts for the susceptibility function are related to each other by means of a set of generalized Kramers-Kronig relationships which are a consequence of the principle of causality. This work has been published in the J. Phys. Chem. (362).

5. Long memory, fractal statistics and Anderson localization for one-dimensional reaction-convection chemical patterns with random propagation velocities

The paper deals with the theory of multicomponent one-dimensional reaction-convection chemical patterns characterized by time-dependent but space-independent propagation velocities. If the propagation velocity is a deterministic function of time then an analytical solution for the time and space dependence of the concentrations of the different chemicals making up the system is obtained. This solution establishes a connection between the concentration fields in an inhomogeneous system and the solutions of the deterministic kinetic equations corresponding to the case when the process is operated in a homogeneous system. If the dynamical behavior of the homogeneous system is given by a stable limit cycle then the reaction intermediates in the inhomogeneous system generate stationary periodic chemical patterns. The theory is used for evaluating the influence of small random perturbations of the propagation speed on the shape of chemical patterns; explicit computations are performed in the case of non-Markovian Gaussian perturbations of the velocity field. It is shown that the random variations of the propagation speed lead to Anderson localization: a limit cycle in the homogeneous system corresponds to a chemical pattern damped in space in the inhomogeneous system. Both analytic and numeric calculations show that the Anderson localization of the concentration patterns is very strong for non-Markovian fluctuations with long memory characterized by correlation functions of the negative power law type. For infinite memory the attenuation factors are Gaussian. For self-similar fractal random processes with long, but finite memory the localization is less strong and the attenuation factor is given by a compressed exponential and has a shape intermediate between a Gaussian and an exponential. Finally for Markovian or independent random processes the localization is weak and the attenuation is exponential. An experiment for testing the predicted theoretical results are suggested and the possibilities of generalizing the theory for reaction-convection systems with thermal fluctuations and for Lévy noise by using the Shlesinger-Hughes renormalization

technique are discussed. This work has been published in Phys. Rev. E. (364).

6. Dynamics and dissipation in an externally forced system

The influence of external perturbation on the bifurcating Selkov model is being studied. One dimensionless parameter, κ which appears multiplicatively in the corresponding chemical kinetic equations, is varied. The parameter κ divides the stability phase diagram into three regions: an oscillatory region, a stable node region and a saddle region. The effect of this parameter on the dynamics of the system when allowed to vary periodically and randomly among the stability regions is studied. When the variations of κ are periodic in time, the system responds with mixed mode oscillations in the case where the forcing frequency is different from the frequency of the oscillations without any perturbations. When the frequencies are equal, the system responds to the forcing by oscillating with the same frequency of the forcing but with a higher amplitude linearly proportional to the amplitude of the perturbation. In the second case, κ varies randomly in time. The dynamics are described by stochastic differential equations. The computed ensemble average exhibits a decay or localization of the limit cycle for small amplitudes of the noise. This decays is faster when the amplitude of the noise is higher. The frequency of the damped oscillations is close to the frequency of the oscillator without noise. As the noise increases, chaotic behavior begins to appear. A stochastic complex Ginzburg-Landau equation is derived using normal form transformations. In the case of very weak noise, a linear phase approximation and the equations for the radial and the phase components of the amplitude separate are used, and can be solved exactly. It is shown that the radial part tends to a fixed value for long times. However, the phase is found to be a Gaussian random variable with time dependent mean and variance. For larger noise amplitudes, different approximations of the phase equations are used where to obtain a closed form for the solution. For noise amplitudes high enough to push the system away from the oscillatory region, the system exhibits high amplitude intermittent bursts in the concentrations for different realizations of the noise; on the other hand, in this case, the average concentrations also exhibit intermittent bursts but with smaller amplitude relative to the aforementioned case. This behavior may be due to a continuous random flips of the system when the parameter κ varies randomly between the saddle and focus regions. The chemical entropy production for all the cited cases was computed. When κ varies periodically with the same frequency, the entropy production increases nonlinearly with the amplitude of the noise; the amplitude of the oscillations increases only linearly with the amplitude of the forcing. In general, when the system is periodically forced, strips of high dissipation and valleys of low

dissipation exists in the space formed by the amplitude of the perturbation and winding number. In the second case, where κ is random, the ensemble average of the entropy production was computed and integrated over time. The overall average entropy production is insensitive to the amplitude of the noise as long as κ does not cross the oscillatory region. When κ begins to cross, the average entropy production increases almost linearly with the amplitude of the noise. This work has been submitted for publication in the J. Chem. Phys. (372).

7. Fluctuation dynamics, thermodynamic analogies and ergodic behavior for nonequilibrium independent rate processes with dynamical disorder

The stochastic properties off the sojourn times attached to a Markov process in continuous time and with a finite number of states are described by using a statistical ensemble approach. This approach is applied for investigating the large time behavior of independent rate processes with dynamical disorder. The large time behavior of the system is described in terms of an effective transport operator which can be expressed as a static average with respect to the stochastic properties off the sojourn times. The method is illustrated by a generalization of the Van den Broeck approach to the generalized Taylor diffusion. Explicit formulas for the effective transport coefficients and for the fluctuations of the concentration fields are derived. The results are used for extending the non-equilibrium generalized thermodynamic formalisms suggest by Keizer and by Ross, Hunt and Hunt, to systems with dynamical disorder. It is shown that the logarithm of the probability density functional concentration fluctuations is a Lyapunov functional of the effective transport equation. This Lyapunov functional plays the role of a generalized nonequilibrium thermodynamic potential which may serve as a basis for a thermodynamic description of the average behavior of the system. The existence and stability o a steady state can be expressed as an extremum condition for the Lyapunov functional. For Taylor diffusion in an external electric field different from zero the generalized potential has a structure similar to the Helmholtz free energy rather than to the entropy. A generalized chemical potential is derived as the functional derivative of the Lyapunov functional with respect to the concentration field; the gradient of this generalized chemical potential is the driving force which determines the structure of the effective transport equation. This work has been published in Physica A (352).

8. Jump statistics, sojourn times, fluctuation dynamics and ergodic behavior for Markov processes in continuous time with a finite number of states

A general approach is introduced for describing the time evolution of a Markov process in continuous time and with a finite number of states. The total number of transition events from one state to other states and of the total

sojourn times of the system in the different states are used as additional state variables. The large time behavior of these two types of stochastic state variables is investigated analytically by using a stochastic Liouville equation. It is shown that the cumulants of first and second order of the state variables increase asymptotically linearly in time. A set of scaled sojourn times is introduced which in the limit of large times have a Gaussian behavior. For long times the total average sojourn times are proportional to the stationary state probability of the process sand, even though the relative fluctuations decrease to zero, the relative cross correlation functions tend towards finite values. The results are used for investigating the connections with Van Kampen's approach for investigating the ergodic properties of Markov processes. The theory may be applied for studying fluctuation dynamics in stochastic reaction diffusion systems and for computing effective rates and transport coefficients for nonequilibrium processes in systems with dynamical disorder. This work has been published in Physica A. (353).

9. Linear free energy relations and reversible stretched exponential relaxation kinetics in systems with static or dynamical disorder

Stretched exponential relaxation is the result of the existence of a large number of relaxation channels, any of them having a very small probability of being open. It is shown that the stretched exponential kinetics obeys a relation of the linear free energy type. The configurational entropy generated by the random distribution of channels is a linear function of the activation energy of the channel with the slowest relaxation rate and highest energy barrier. This property of stretched exponential relaxation is used for studying multichannel first-order relaxation kinetics of reversible processes. By combining the linear free energy relationship with the principle of detailed balance a generalized kinetic law of the stretched exponential type is derived. This work has been published in J. Phys. Chem. (367).

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PERSONNEL PARTICIPANTS-RECEIVED Ph.D. DURING THE DATES OF THIS PROJECT

Dr. Sergey Samoilov, title of thesis: "Reconstruction and Functional Analysis of General Chemical Reactions and Reaction Networks", 09/97.
Dr. Ian Millett, title of thesis: "Alternatives to Quenching in Complex Dynamical Systems", 12/98.
Dr. Alexander Gilman, title of thesis: "Searching for Chemical Reaction Mechanisms with Genetic Algorithms, 01/99.

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****marks publications accredited to AFOSR**

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